Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of bimagnetic ionic liquid and application for selective aerobic oxidation of aerobic alcohols under mind conditions

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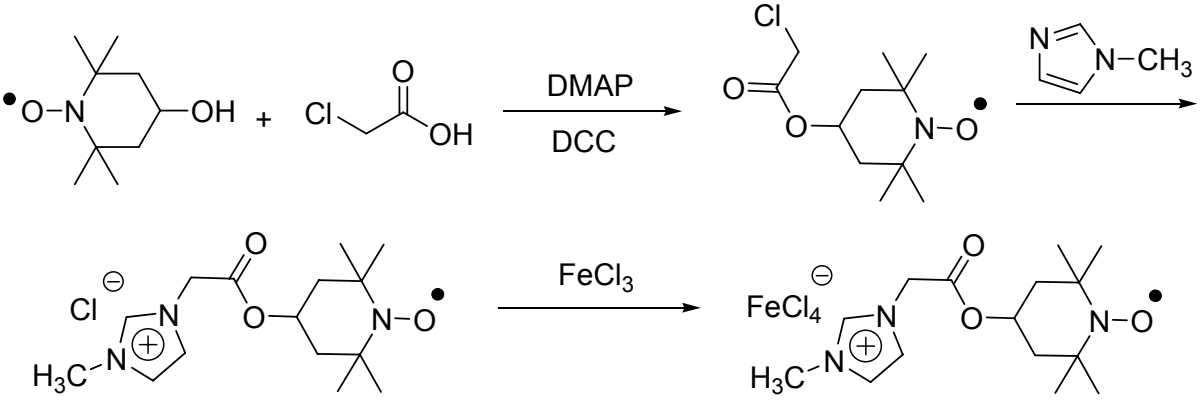
Supporting information

1. General information

The 4-hydroxy-TEMPO, chloroacetic acid, 1-methylimidazole and $FeCl_3$ were purchased from J&K CHEMICA. The other organic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

NMR spectra were recorded on a Bruker 300 or 400 spectrometer in $CDCl_3$. ^1H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^1H and ^{13}C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector. Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum as eluent. The EPR experiments were performed on a Bruker EMX-6 with the following condition: microwave frequency 9.86 GHz, microwave power: 20.0 mW, center field 3520 G, magnetic field range 3520 G, modulation amplitude 2.00 G, time constant 10.24 ms, and receiver gain 2.00e+005. The magnetic properties were investigated by a superconducting quantum interference device (SQUID, Quantum Design MPMS-XL-5) using approximately 10 mg to 20 mg of the sample. The Raman spectrum experiment was performed by HORIBA Jobin Yvon (HR800 UV).

2. Synthesis and characterization of the bimagnetic ionic liquid



Synthesis of the bimagnetic ionic liquid: To a stirred solution of 4-hydroxy-2,2,6,6-tetramethylpiperdine-1-oxyl (4.3 g, 25 mmol) and chloroactic acid (2.0 g, 25 mmol) in CH_2Cl_2 (80 mL) at 0 ^oC under argon, DCC (1, 3-dicyclohexylcarbodiimide, 5.15 g, 25 mmol) and DMAP (4-dimethylaminopyridine, 0.75 g, 6.25 mmol) were dropwise added. And the mixture was stirred for 12 h at room temperature. After reaction, the precipitate was filtered, and the filtrate was consecutively washed with 1 M HCl (25 mL), saturated $NaHCO_3$ (50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure. Further purification was made through a short flash chromatography (the eluent: EtOAc-petroleum ether 1:10) providing 2,2,6,6-tetramethyl- 1-oxyl-piperidin-4-yl 2-chloroacetate as a red powder. Then 1-methylimidazole (0.46 g, 5.6 mmol) was added to a solution of 2,2,6,6-tetramethyl- 1-oxyl-piperidin-4-yl 2-chloroacetate (1.00 g, 4 mmol) in MeCN (30 mL), and the resulting solution was stirred for 48 h at 80 ^oC. After concentration to about half the original volume, diethyl ether was added to get a precipitate. Then the solid was filtered and washed with acetone, diethyl ether, successively to give [Imim-TEMPO][Cl] as a light red powder. By mixing equimolar amount of [Imim-TEMPO][Cl] and anhydrous $FeCl_3$

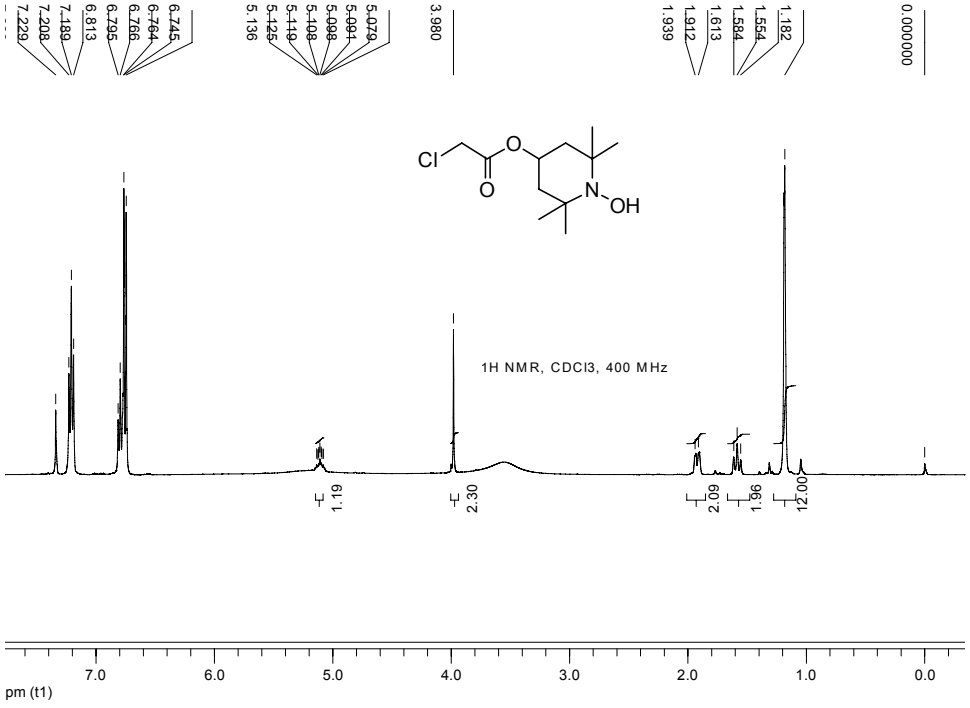
under argon atmosphere in anhydrous acetone, rude [Imim-TEMPO][$FeCl_4$] was obtained after evaporation under reduced pressure. Finally the powder of [Imim-TEMPO][$FeCl_4$] was obtained after drying for 72 h at 80 ^oC in vacuum.

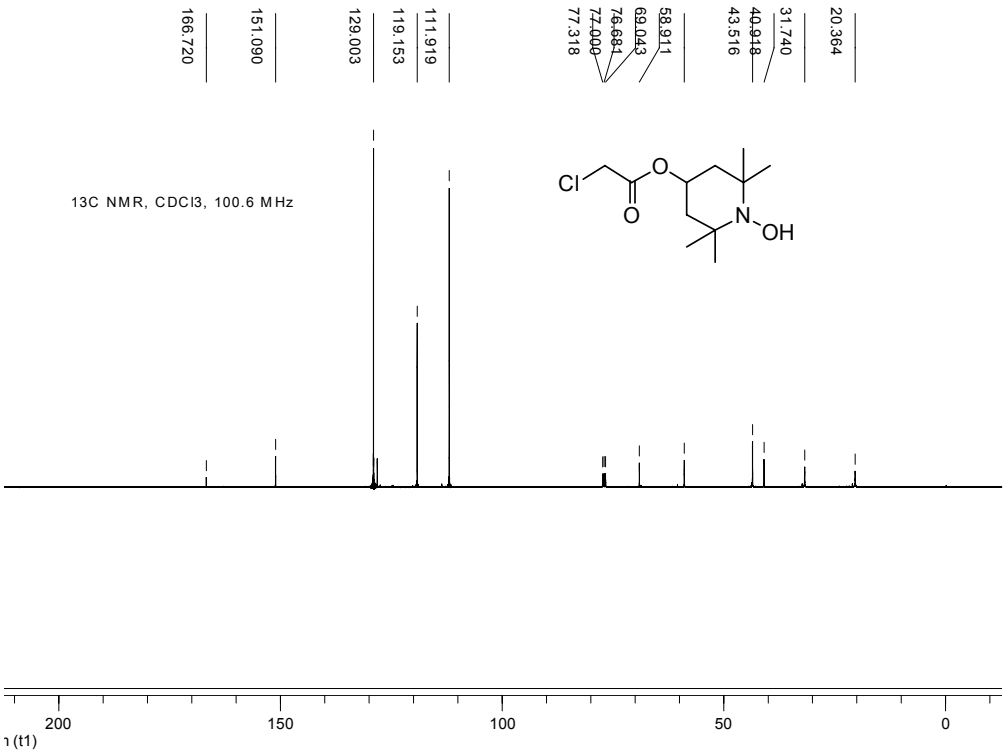
2, 2, 6, 6-tetramethyl- 1-oxyl-piperidin-4-yl 2-chloroacetate**:** ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC): δ =1.18 (s, 12 H, CH_3), 1.58 (t, ^3J(H,H) = 12 Hz, 2 H; CH_2), 1.93 (d, ^3J(H,H) = 5.4 Hz, 2 H), 3.98 (s, 2 H), 5.08-5.14 (m, 1 H); ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$, 25 ^oC): δ = 20.4, 31.7, 40.9, 43.5, 58.9, 69.0, 166.7.

[Imim-TEMPO][Cl]: ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC): δ 1.13 (s, 12 H), 1.37 (t, ^3J(H,H) = 9 Hz, 1H), 1.59 (t, ^3J(H,H) = 9 Hz, 2 H), 1.96 (t, ^3J(H,H) = 9 Hz, 2H), 3.98 (s, 3H), 5.05 (s, 1H), 5.11-5.21 (m, 2H), 7.40 (s, 2H); ^{13}C {^1H} NMR (100.6 MHz, $CDCl_3$): δ = 20.8, 29.8, 36.0, 42.2, 50.0, 60.2, 70.0, 123.5, 123.6, 128.4, 167.4.
mp 213-216 ^oC; ESI-MS (4.8 kV): m/z (%): 295 (100) $[M]^+$.

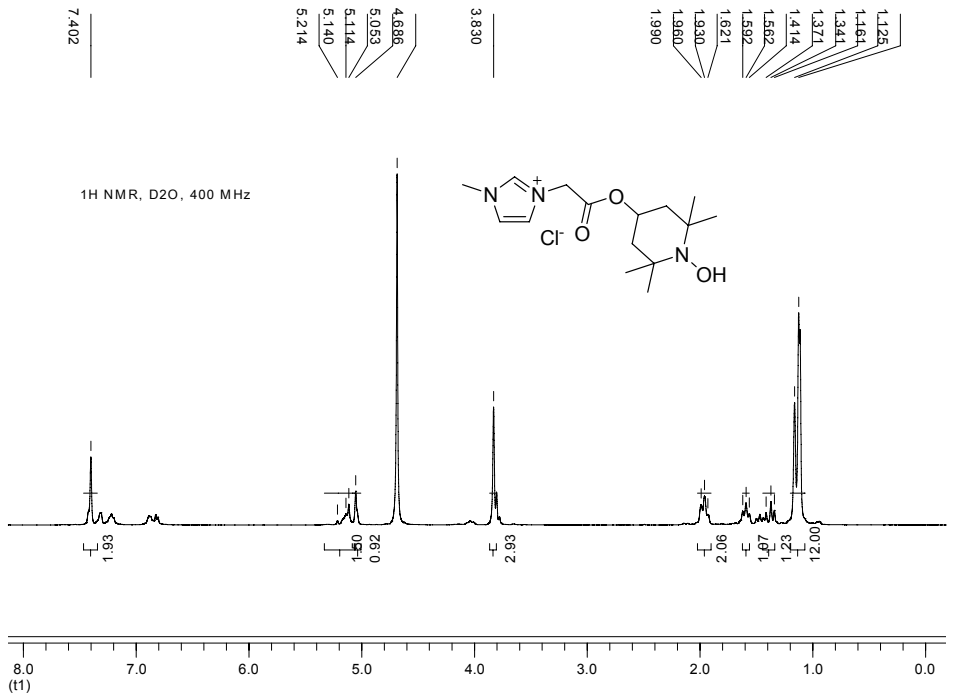
[Imim-TEMPO][$FeCl_4$]: mp 113-116 ^oC, ESI-MS (4.8 kV): m/z (%): 295 (100) $[M]^+$. ESI-MS (4.8 kV): m/z (%): 197 (100) $[M]^-$. Anal. Calcd for $C_{15}H_{25}Cl_4FeN_3O_3$: C 36.54, H 5.11, N 8.52. Found: C 37.07, H 4.71, N 8.32.

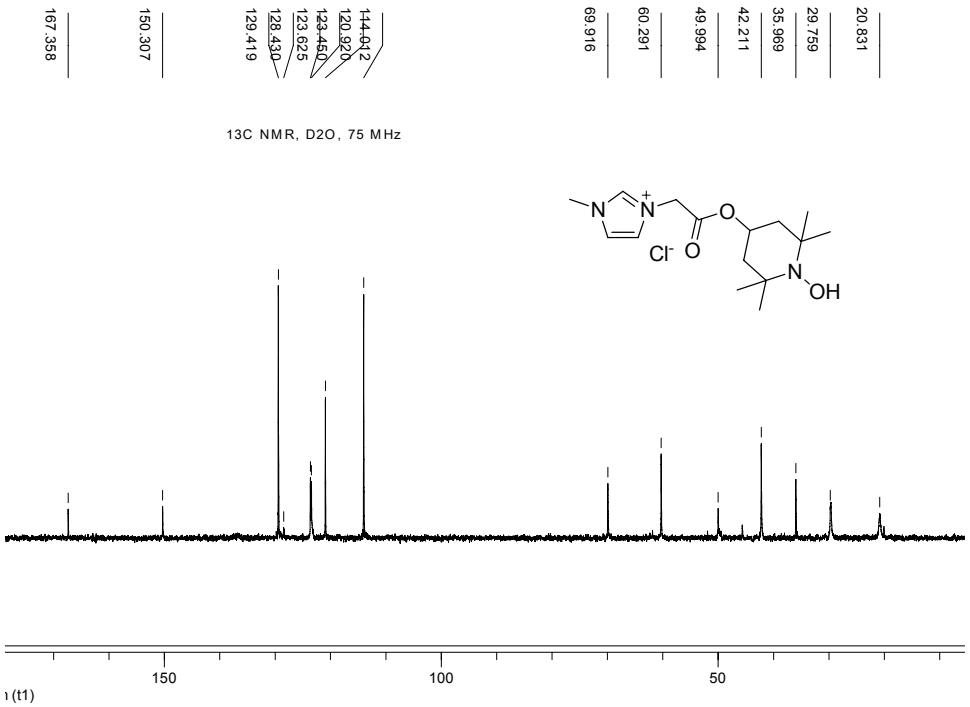
^1H NMR and ^{13}C NMR for 2, 2, 6, 6-tetramethyl- 1-oxyl-piperidin-4-yl 2-chloroacetate

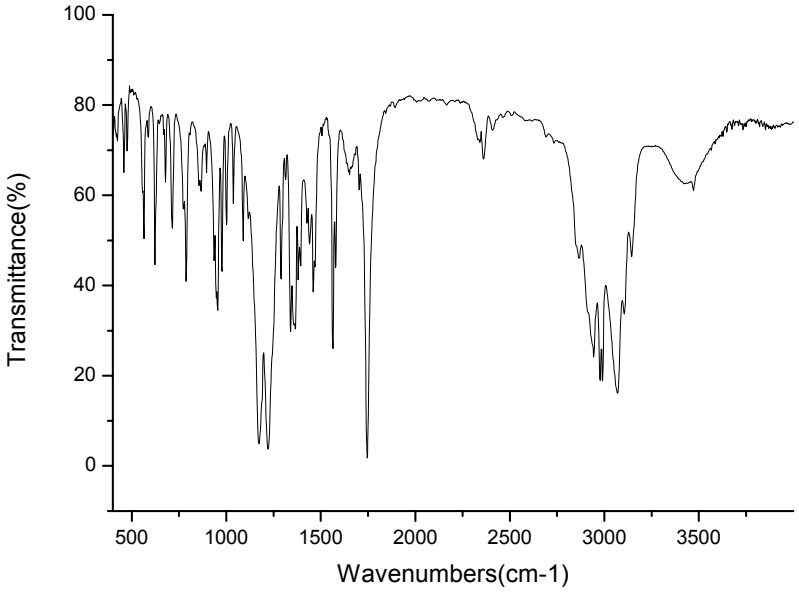



166.720
151.090
129.003
119.153
111.919
77.318
77.000
76.681
69.043
58.911
43.516
40.918
31.740
20.364
13C NMR, CDCl3, 100.6 MHz
Cl
O
O
N
OH
200
150
100
50
0
1 (t1)

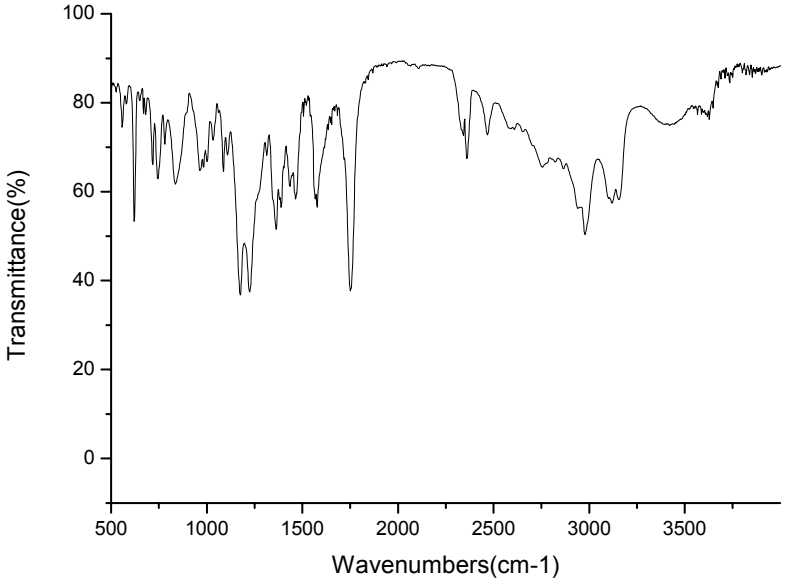
^{1}H NMR and ^{13}C NMR for [Imim-TEMPO][Cl]



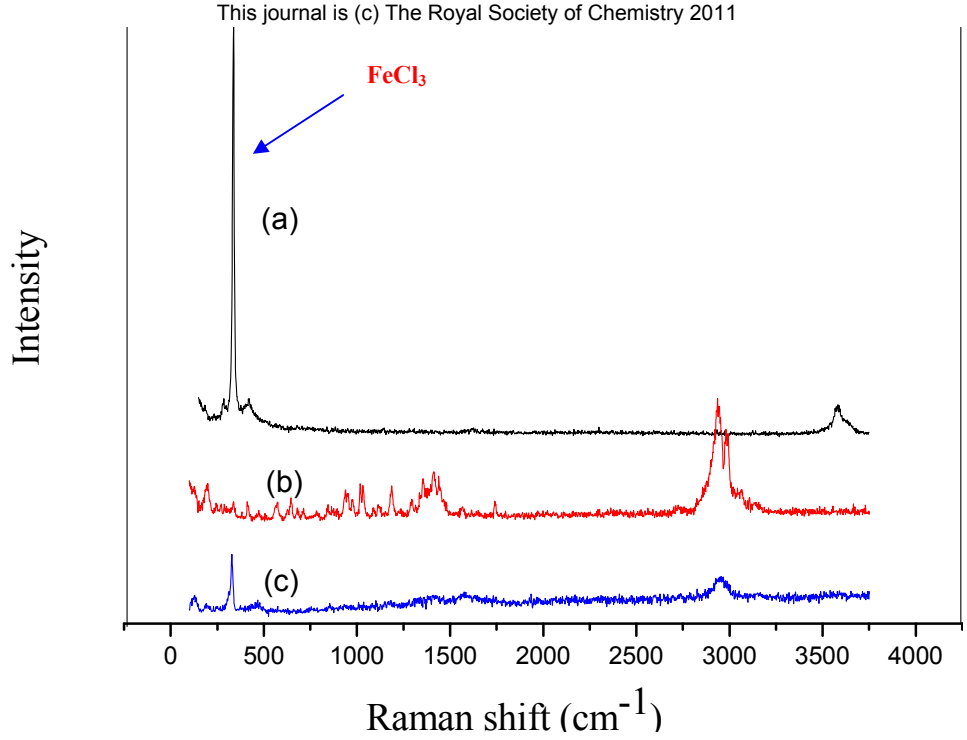




Infrared absorption spectrum for [Imim-TEMPO][Cl]



Infrared absorption spectrum for [Imim-TEMPO][$FeCl_4$]

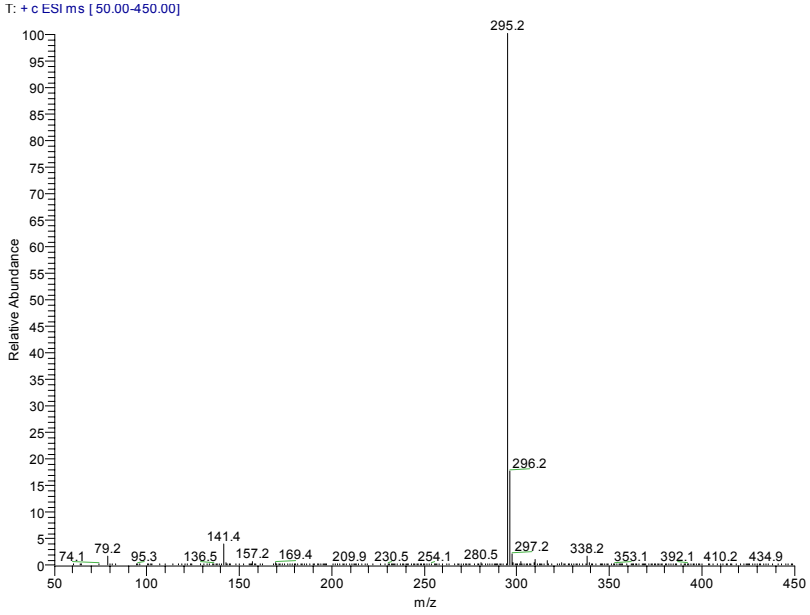


Raman spectrum of (a) $FeCl_3$ (b) [Imim-TEMPO][Cl] and (c) [Imim-TEMPO][$FeCl_4$]

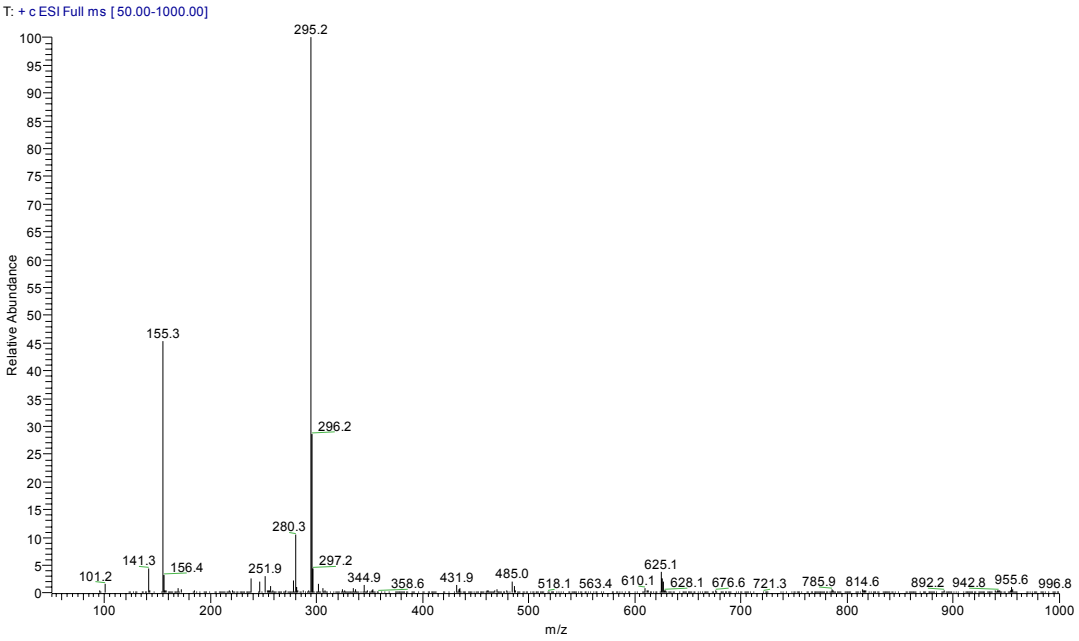
We measured the Raman spectra of [Imim-TEMPO][$FeCl_4$] so as to obtain information about the anion structure and the spectrum showed a strong band at 330 cm^{-1}, which is already reported and is assigned to the totally symmetric Fe-Cl stretch vibration of $FeCl_4^-$.

The ESI-MS spectrum of [Imim-TEMPO][Cl] and [Imim-TEMPO][$FeCl_4$]

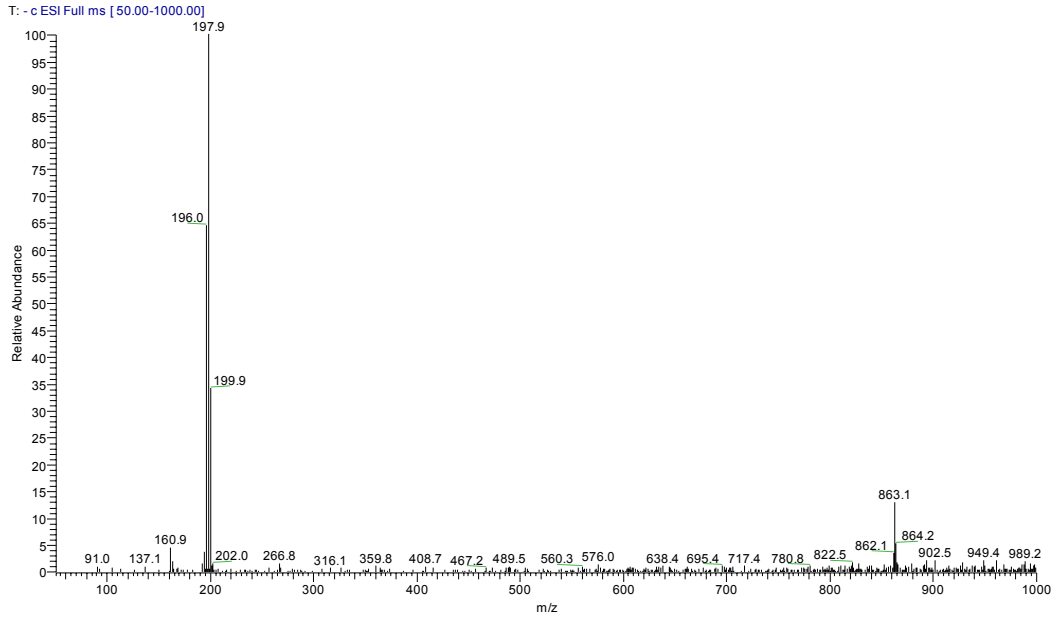
[Imim-TEMPO][Cl]: ESI-MS (4.8 kV): m/z (%): 295 (100) $[M]^+$.



[Imim-TEMPO][$FeCl_4$]: ESI-MS (4.8 kV): m/z (%): 295 (100) $[M]^+$.



[Imim-TEMPO][$FeCl_4$]: ESI-MS (4.8 kV): m/z (%): 197 (100) $[M]^-$.

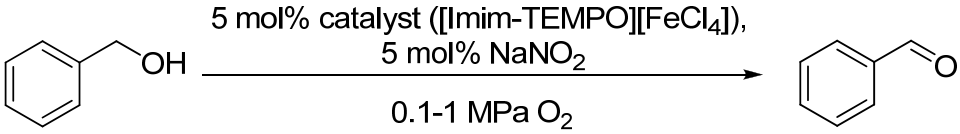


3. Typical procedure for the aerobic oxidation of aromatic alcohols catalyzed by bimagnetic ionic liquid

A mixture of substrate (1.93 mmol), [Imim-TEMPO][$FeCl_4$] (5 mol%), $NaNO_2$ (5 mol%) was added into a 25-mL autoclave equipped with an inner glass tube. 0.2 MPa O_2 was introduced into the autoclave and the reaction system was heated to the desired temperature. The mixture was then stirred continuously for the designated reaction time. After cooling, products were extracted by diethyl ether, and analyzed by gas chromatography (Shimadzu-2104) equipped with a capillary column (RTX-5 30m×0.25μm) using a flame ionization detector. The structure and the purity of the products were further identified using NMR (Bruker-300 MHz and 400 MHz), GC-MS (HP G 1800 A), HPLC–MS (LCQ Advantage) and GC, HPLC by comparing reaction times and fragmentation patterns with those of authentic samples.

4. Supporting Table

Table S1. Aerobic oxidation of benzyl alcohol catalyzed by bimagnetic ionic liquid[a]



Entry	Catalyst ([Imim-TEMPO][Cl]) loading [%]	T [°C]	t [h]	Po_2 [MPa]	Conv. [%][b]	Yield [%][b]
1	0	30	1	1	0.4	0.3
2	5	30	1	0	1	1
3[c]	5	30	1	1	1	1
4[d]	5	30	1	1	0.5	0.5
5[e]	5	30	1	1	0	0
6	5	30	2	1	100	99
7	5	30	1	1	73	72
8	5	30	1	0.6	70	69
9	5	30	1	0.2	70	70
10	5	30	24	0.1	100	99
11[f]	5	30	48	0.1(air)	65	63
12	5	60	0.5	0.2	62	62
13[g]	5	20	12	0.2	85	79
14	5	30	1.5	0.2	100	99
15[h]	-	30	1	0.2	100	99
16[i]	5	30	1	0.2	49	47
17[j]	5	30	1	0.2	0.3	0.3
18	1	30	10	0.2	32	30

[a] Reaction conditions: Benzyl alcohol (0.2 mL, 1.93 mmol), $NaNO_2$ (6.7 mg, 0.097 mmol). [b] Determined by GC using biphenyl as an internal standard. [c] Without $NaNO_2$. [d] [Imim-TEMPO][Cl] instead of [Imim-TEMPO][$FeCl_4$] as catalyst. [e] [Imim][FeCl4] instead of [Imim-TEMPO][$FeCl_4$] as catalyst. [f] Air as the oxygen resource. [g] 3.9 % of acid as the byproduct was formed. [h] $FeCl_3$ (0.016 g, 0.097 mmol), TEMPO (0.015 g, 0.097 mmol), $NaNO_2$ (6.7 mg, 0.097 mmol). [i] 0.3 ml H_2O was added. [j] 0.3 ml 1-butyl-3-methylimidazolium chloride [Bmim][Cl].

Table S2. Aerobic oxidation of *n*-heptanol catalyzed by bimagnetic IL was inert under the following conditions[a]

Entry	Catalyst ([Imim-TEMPO][Cl]) loading [%]	T [^{o}C]	t [h]	Po_2 [MPa]
1	5	30	14	0.2
2	5	100	14	0.2
3	10	30	14	0.2
4	5	30	14	1
5[c]	5	30	14	0.2

[a] Reaction conditions: *n*-heptanol (1.93 mmol), $NaNO_2$ (6.7 mg, 0.097 mmol), V_{H2O} = 0.3 mL. [b] Determined by GC using biphenyl as an internal standard. [c] Cinnamyl alcohol instead of *n*-heptanol.

Table S3. The comparison of effective magnetic moment

Entry	Compound	μ_{eff} (μ_B)	Ref.
1	$FeCl_3$	5.92	[1]
2	TEMPO	1.73	[2]
3	[Imim-TEMPO[Cl]	1.39	-
4	[Imim-TEMPO[$FeCl_4$]	6.66	-

References: [1] S. Hayashi, H. Hamaguchi, *Chem. Lett.,* 2004, **33**, 1590. [2] Y. Yoshida, H. Tanaka, G. Saito, *Chem. Lett.,* 2007, **36**, 1096.

4. Supporting Figures

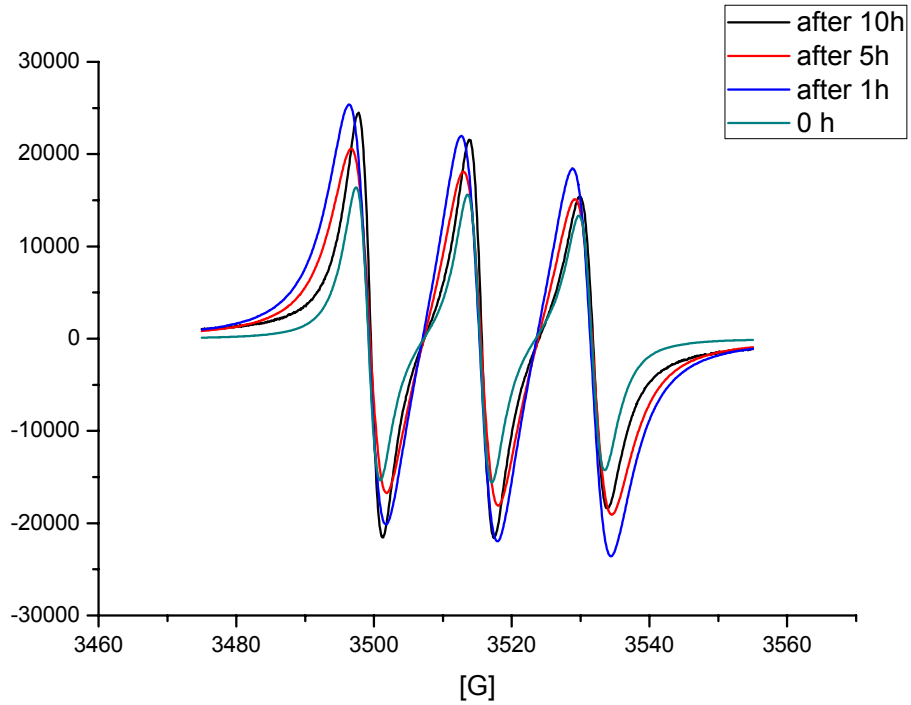
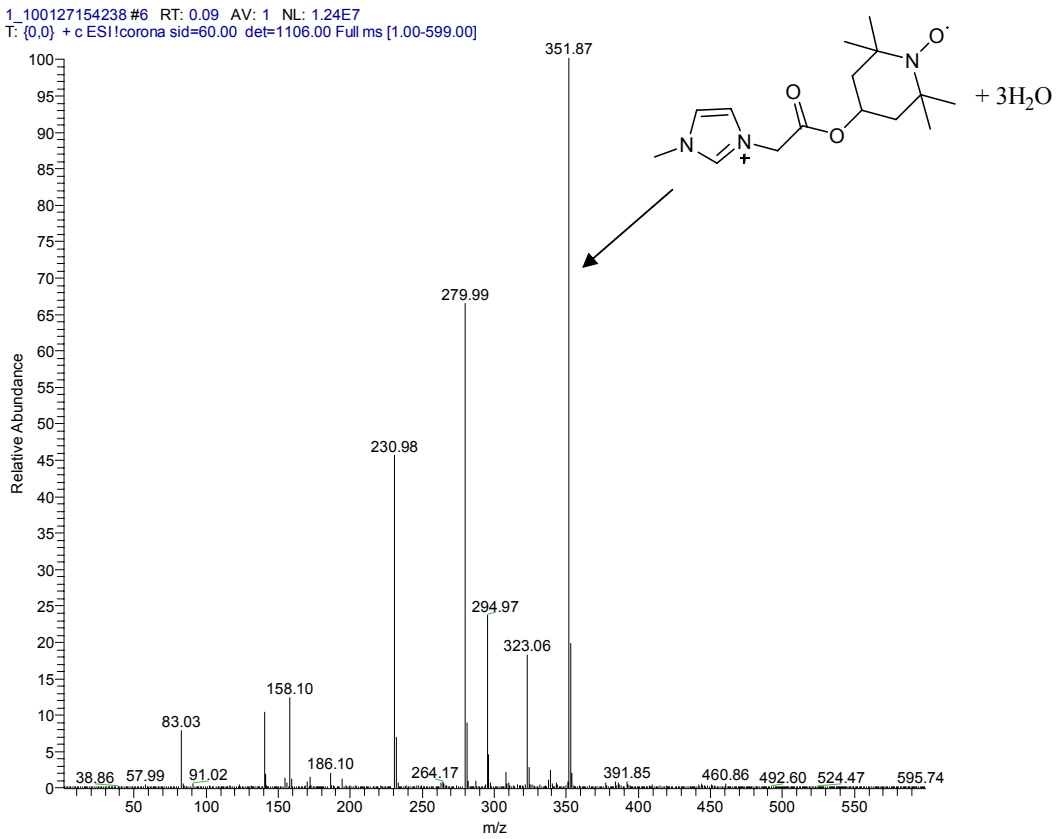
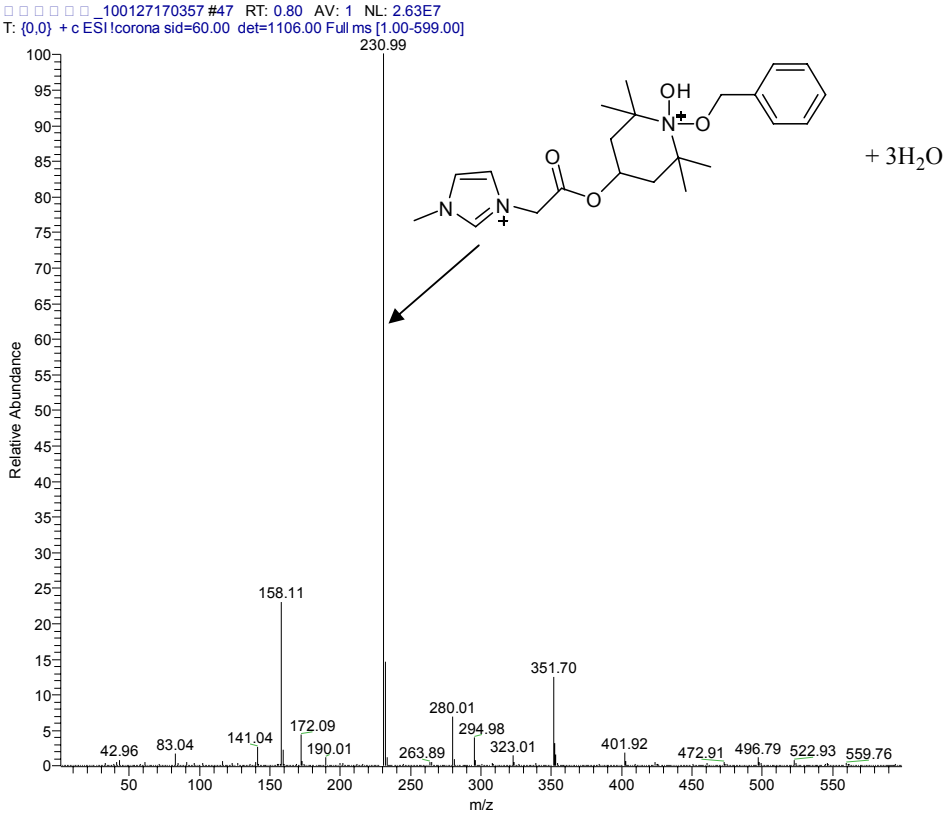


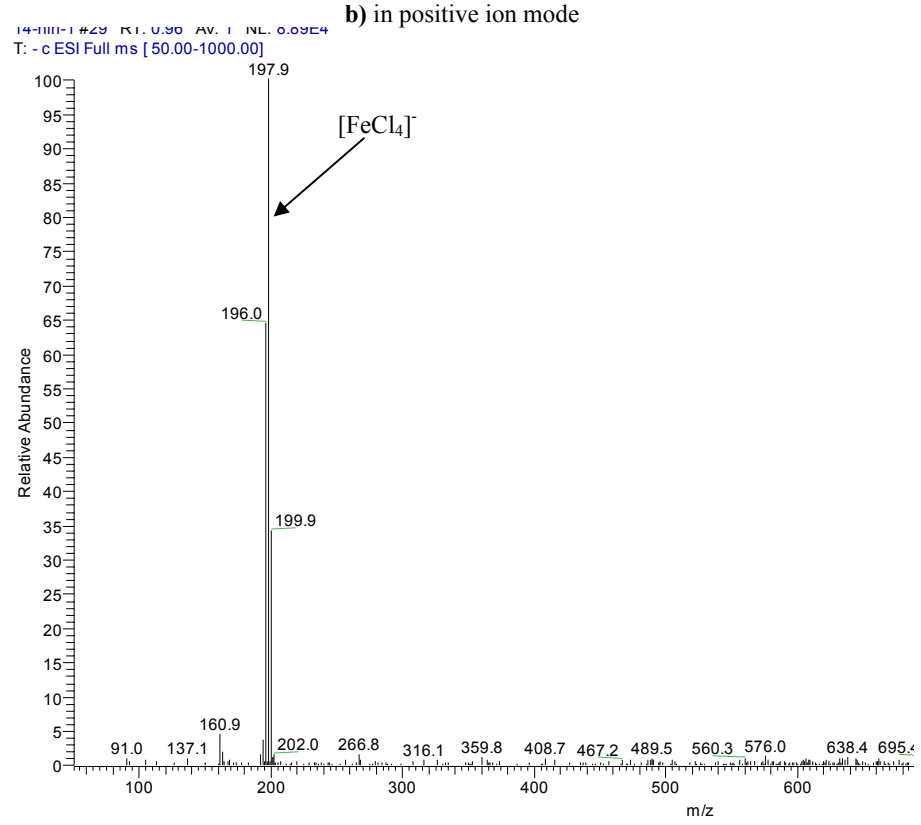
Figure S1. EPR experiments. Conditions: Benzyl alcohol (0.5 ml, 4.83 mmol), Catalyst ([Imim-TEMPO][$FeCl_4$]) (5 % mmol), $NaNO_2$ (5 % mmol), Temperature 30°C, O_2 (0.1 MPa).



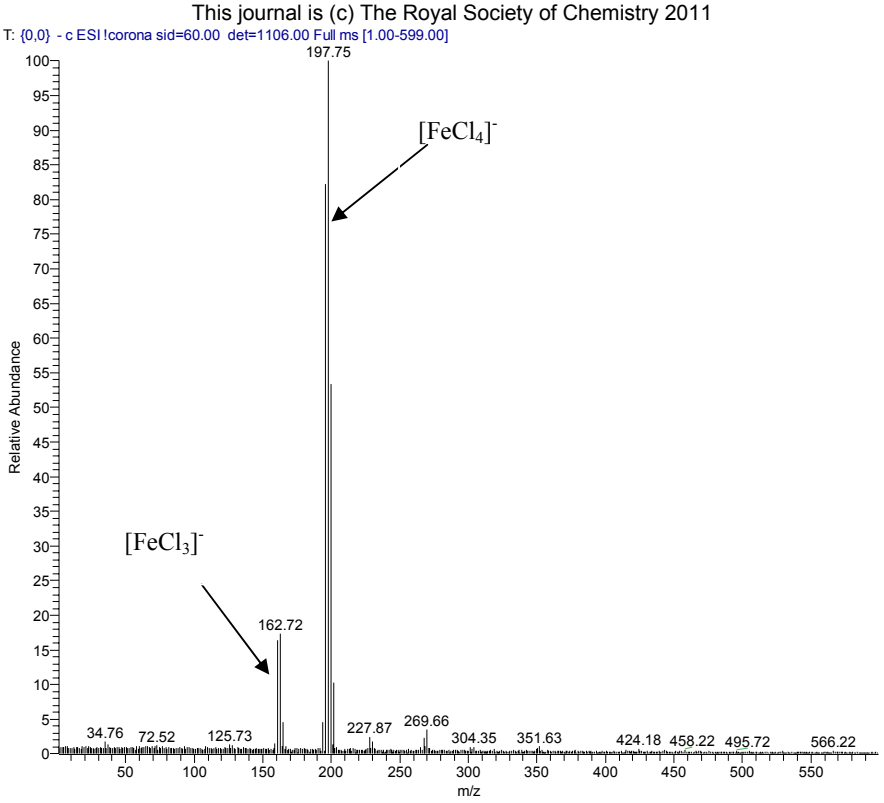
a) in positive ion mode



b) in positive ion mode



c) in negative ion mode



d) in nagtive ion mode

Figure S2. ESI-MS experiment. Reaction conditions: Benzyl alcohol (0.5 ml, 4.83 mmol), Catalyst ([Imim-TEMPO][$FeCl_4$]) (2.5 % mmol), $NaNO_2$ (2.5 % mmol), Temperature 60°C, O_2 (0.1 MPa) Time (2 h). **a**) without adding $NaNO_2$; **b**) 2 h after adding $NaNO_2$; **c**) without adding $NaNO_2$; **d**) 2 h after adding $NaNO_2$.

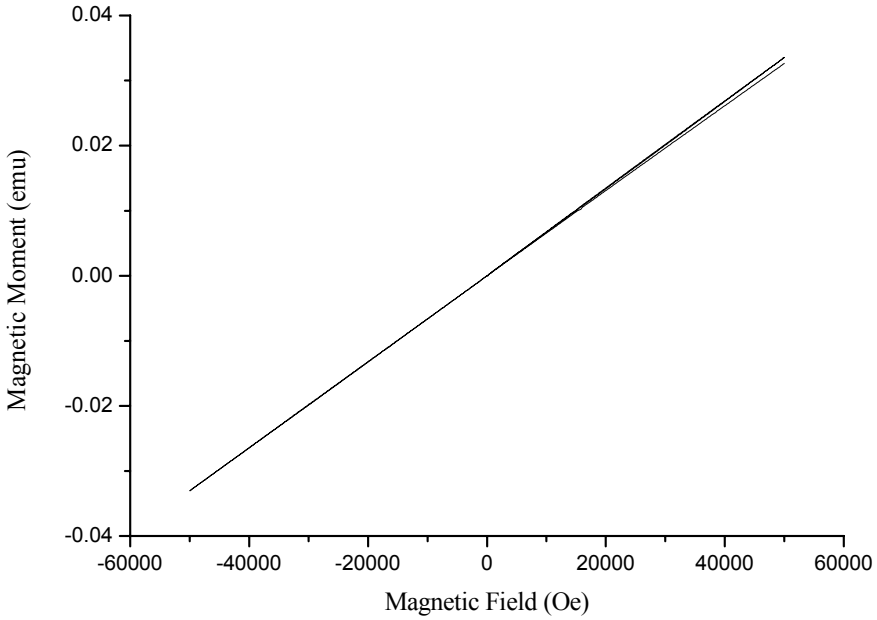


Figure S3. Field dependence of the magnetic moment for [Imim-TEMPO][$FeCl_4$] at 298 K.

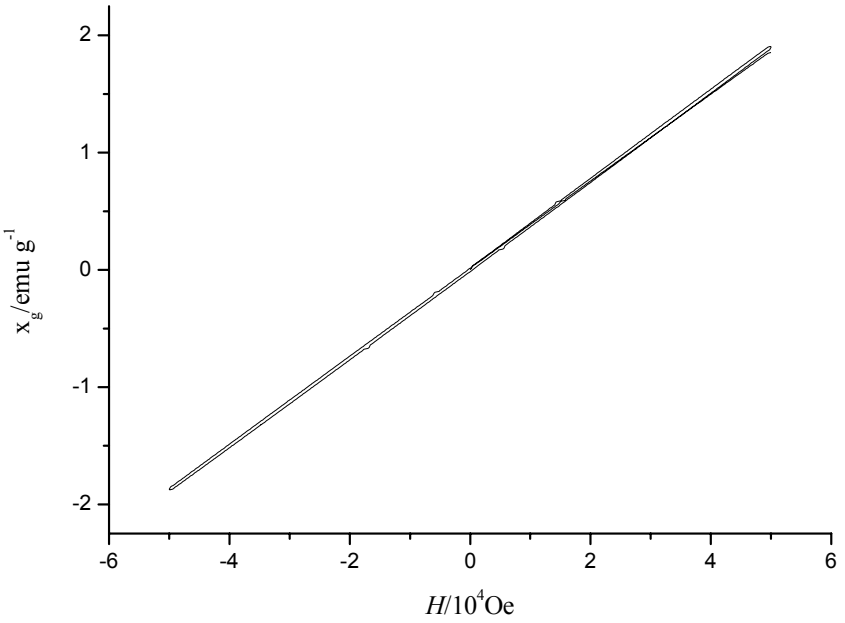


Figure S4. Field dependence of the mass susceptibility χ_g for [Imim-TEMPO][$FeCl_4$] at 298 K.

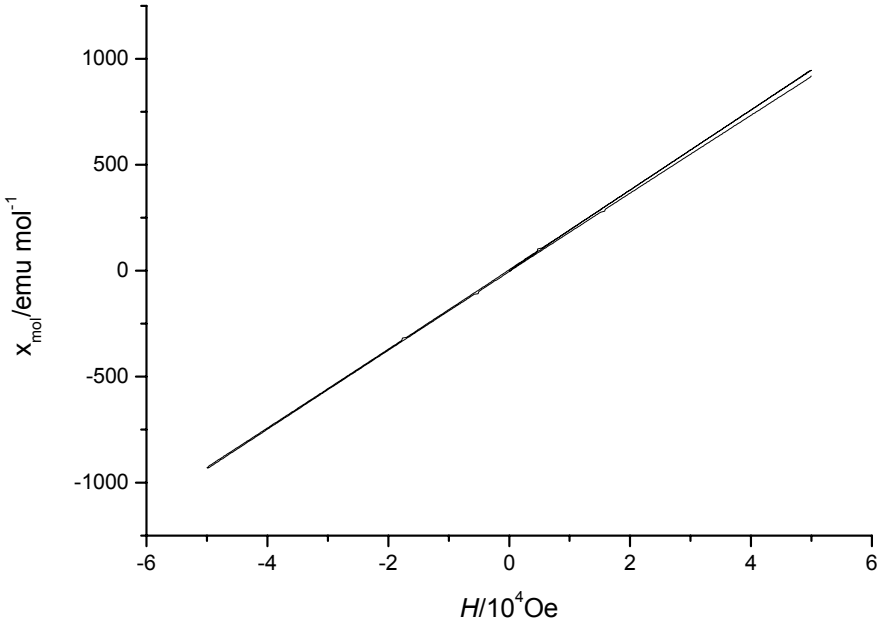


Figure S5. Field dependence of the static molar susceptibility χ_{mol} for [Imim-TEMPO][$FeCl_4$] at 298 K.

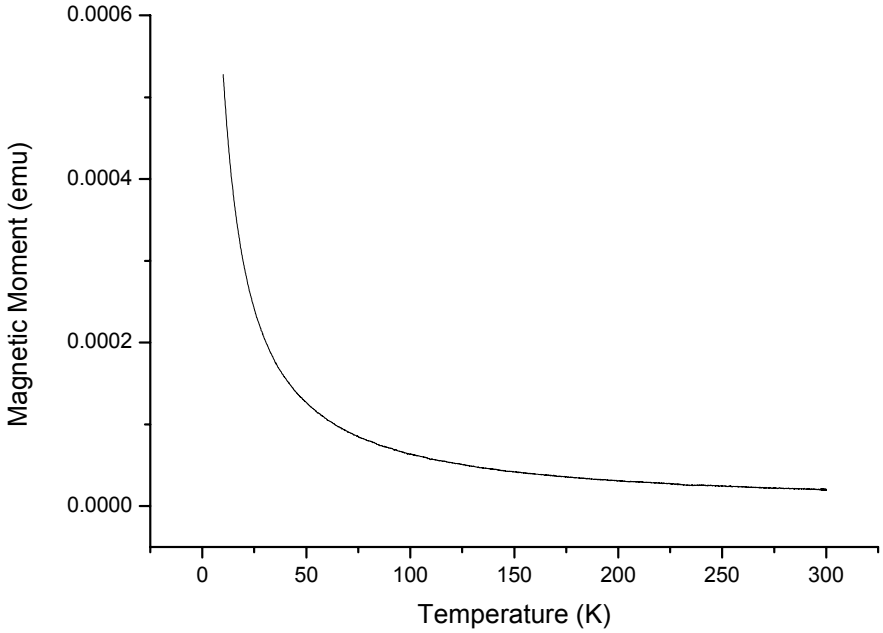


Figure S6. Temperature dependence of the magnetic moment at a field of 500 Oe for [Imim-TEMPO][$FeCl_4$].

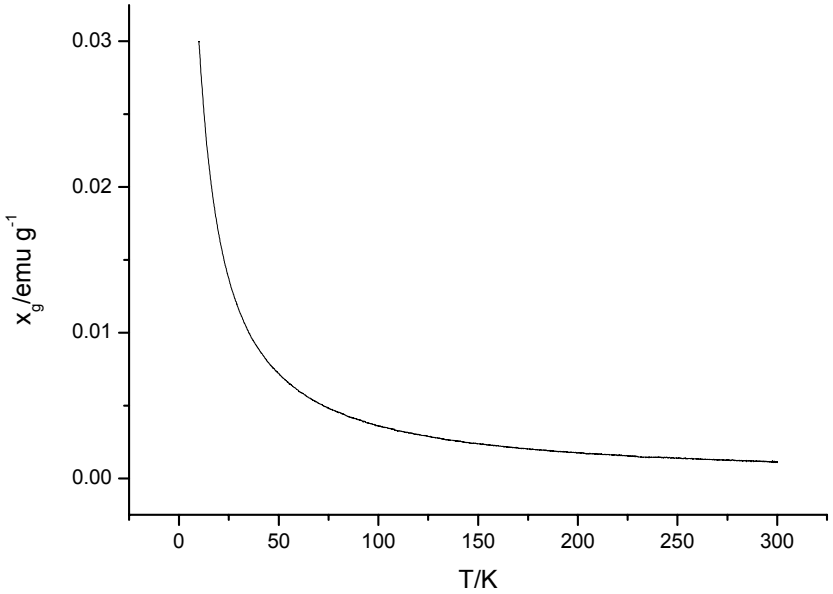


Figure S7. Temperature dependence of the mass susceptibility χ_g at a field of 500 Oe for [Imim-TEMPO][$FeCl_4$].

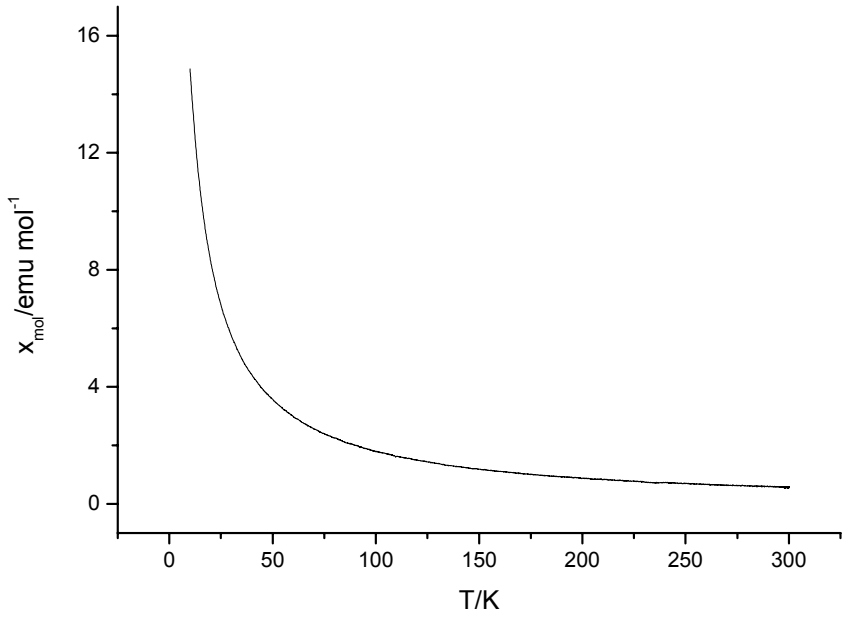


Figure S8. Temperature dependence of the static molar susceptibility χ_{mol} at a field of 500 Oe for [Imim-TEMPO][$FeCl_4$].

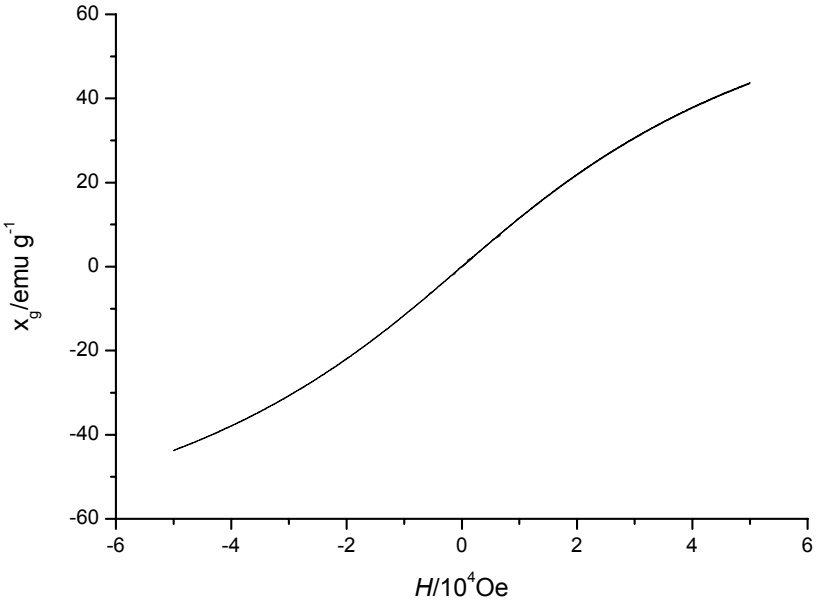


Figure S9. Field dependence of the mass susceptibility χ_g for [Imim-TEMPO][$FeCl_4$] at 5 K.

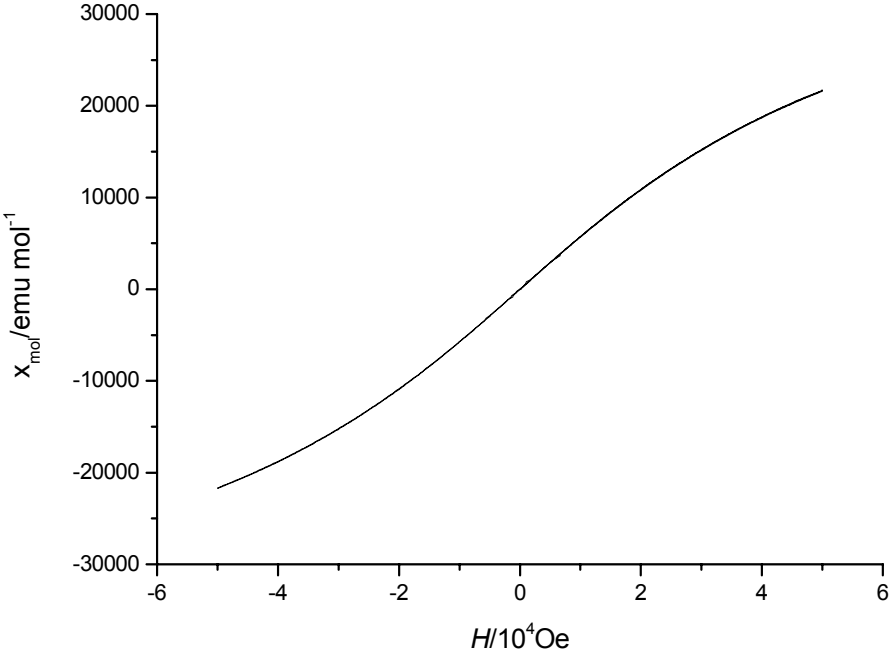


Figure S11. Field dependence of the static molar susceptibility χ_{mol} for [Imim-TEMPO][$FeCl_4$] at 5 K.

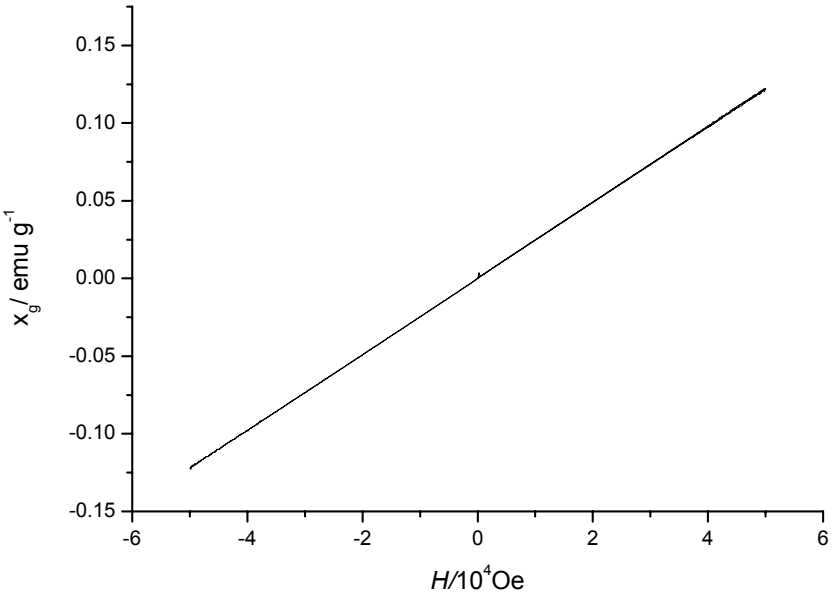


Figure S12. Field dependence of the mass susceptibility χ_g for [Imim-TEMPO][Cl] at 298 K.

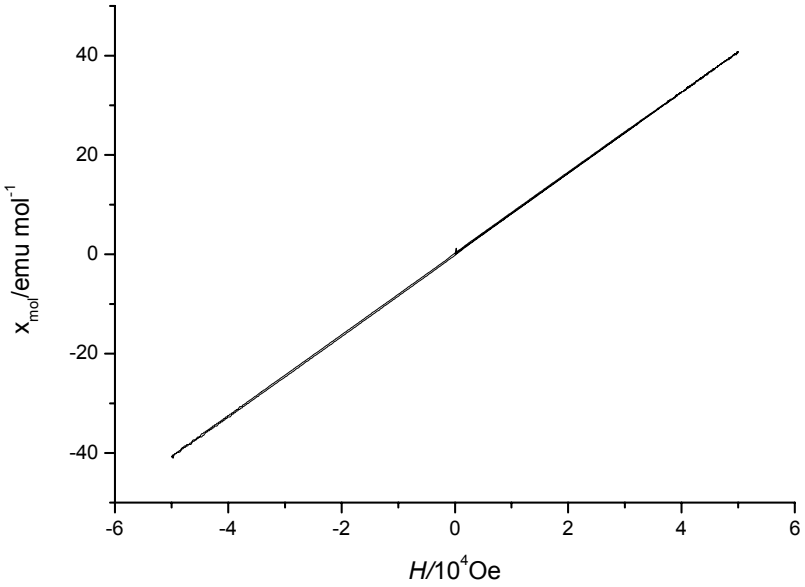


Figure S13. Field dependence of the static molar susceptibility χ_{mol} for [Imim-TEMPO][Cl] at 298 K.

5. The ^{1}H NMR and ^{13}C NMR data for products identification

Benzaldehyde

Light yellow oil liquid, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.50 (t, ^{3}J(H,H) = 7.7 Hz, 2H), 7.60 (t, ^{3}J(H,H) = 7.4 Hz, 1H), 7.84 (d, ^{3}J(H,H) = 7.9 Hz, 2H), 9.98 (s, 1H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C): δ =128.9, 129.6, 134.3, 136.2, 192.3.

4-Methoxy-benzaldehyde

Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.87(s, 3H), 7.00 (d, ^{3}J(H,H) = 8.72 Hz, 2H), 7.82 (d, ^{3}J(H,H) = 8.78 Hz, 5H), 9.87 (s, 1H, CHO); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ= 55.5, 114.3, 130.0, 131.9, 164.6, 190.7.

2-Methoxy-benzaldehyde

Light yellow solid, mp: 36-38 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.84 (s, 3H), 6.94 (m, 2H), 7.48 (t, ^{3}J(H,H) = 8.4 Hz, 1H), 7.75 (d, ^{3}J(H,H) = 3.9 Hz, 1H), 10.4 (s, 1H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 55.4, 111.5, 120.4, 124.6, 128.2, 135.8, 161.6, 189.5.

3-Methoxy-benzaldehyde

Light yellow oil liquid, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.83(s, 3H), 7.14 (m, 1H), 7.36 (d, ^{3}J(H,H) = 1.05 Hz, 1H), 7.42 (m, 2H), 9.94 (s, 1H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 55.3, 112.0, 121.3, 123.4, 129.9, 137.7, 160.1, 192.0.

4-Methyl benzaldehyde

Colorless liquid, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.44 (s, 3H), 7.33 (d, ^{3}J(H,H) = 3.9 Hz, 2H), 7.78 (d, ^{3}J(H,H) = 4.05 Hz, 2H), 9.97 (s, 1H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 21.9, 129.7, 129.9, 134.2, 145.6, 192.0.

4-Nitrobenzaldehyde

Light yellow acicular crystal, mp: 105-106 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.08 (d, ^{3}J(H,H) = 4.35 Hz, 2H), 8.39 (d, ^{3}J(H,H) = 4.35 Hz, 2H), 10.16 (s, 1H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C) : δ = 124.2, 130.4, 140.0, 151.1, 190.2.

2-Nitrobenzaldehyde

Light yellow solid, mp: 45-46 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.78 (m, 2H), 7.96 (d, ^{3}J(H,H) = 2.7 Hz, 1H), 8.13 (d, ^{3}J(H,H) = 3 Hz, 1H), 10.43 (s, 1H); ^{13}C {1H} NMR (75 MHz, $CDCl_3$, 25^{o}C): δ = 124.5, 129.6, 131.4, 134.1, 188.1.

Acetophenone

Light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.60 (s, 3H), 7.46 (t, ^{3}J(H,H) = 7.7 Hz, 2H), 7.56 (t, ^{3}J(H,H) = 7.5 Hz, 1H), 7.96 (d, ^{3}J(H,H) = 7.8 Hz, 2H); ^{13}C {^{1}H} NMR ($CDCl_3$, 100.6 MHz, 25^{o}C): δ =26.5, 128.2, 128.5, 133.0, 137.1, 198.1.

Diphenyl-methanone

White crystal, 47-48 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.48 (t, ^{3}J(H,H) = 7.9 Hz, 4H), 7.58 (t, ^{3}J(H,H) = 7.9 Hz, 2H), 7.81 (t, ^{3}J(H,H) =5.7 Hz, 4H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 128.3, 130.1, 132.4, 137.6, 196.7.

Thiophene-2-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$, 25^{o}C): δ = 7.21 (s, H), 7.77 (m, 2H), 9.94 (s, 1H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$, 25^{o}C): δ =128.3, 135.1, 136.3, 143.9, 183.0.